

THE EFFECTS OF CHLOROBENZENE PRE-TREATMENT ON THE LOW-SEVERITY LIQUEFACTION BEHAVIOUR OF PITTSBURGH No.8 COAL

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ABSTRACT

Recent work has demonstrated that pre-treating coals, particularly with polar solvents, can give rise to significantly improved yields under relatively low-severity liquefaction conditions. Although accessibility is undoubtedly improved, interpretation of these phenomena in terms of changes in the macromolecular structure of coals is complicated by the fact some organic matter is being removed at the same time that conformational changes may be occurring. Chlorobenzene has the advantage of extracting virtually no organic matter from coals and, in this study, the effects of chlorobenzene treatment on short contact time tetralin extraction and dry hydrogenation with and without a dispersed sulphided molybdenum (Mo) catalyst for the Pittsburgh No. 8 Argonne Premium Coal Sample have been investigated. While the chlorobenzene treatment significantly improved the yields from tetralin extraction and non-catalytic hydrogenation due to improved accessibility of solvent and hydrogen gas respectively, reduced yields were obtained in catalytic hydrogenation presumably due to the oil diffusing more effectively out of the remaining macromolecular framework and reducing the effectiveness of hydrogen atom transport from the catalyst.

INTRODUCTION

It was established by Brown and Waters ⁽¹⁾ during the 1960s that chloroform-extractable material within the macromolecular structure of coking coals markedly affects their ability to swell during carbonisation. A close correspondence was found between the release of chloroform-soluble material and pore accessibility with increasing temperature. More recently, the effect of pre-swelling and pre-extracting coals in both polar and non-polar solvents on conversions in direct liquefaction has begun to receive considerable attention ⁽²⁻⁷⁾ as it is particularly important to overcome mass transfer limitations to maximise yields. For extraction in hydrogen-donor ⁽²⁻⁵⁾ and non-donor ⁽⁵⁻⁷⁾ solvents and for dry (solvent-free) hydrogenation ⁽⁸⁾, significant improvements in overall conversions to pyridine/tetrahydrofuran (THF)-soluble material and in oil yields have been achieved. The study by Joseph ⁽⁴⁾ in which tetrabutylammonium hydroxide (TBAH) was the most effective swelling solvent used has demonstrated that the beneficial effect is evident in hydroliquefaction both with and without a dispersed catalyst. As well as pre-swelling or pre-extracting coals in polar solvents, contacting coals at elevated temperatures with non-polar liquefaction solvents including 1-methylnaphthalene ⁽⁷⁾ and 9,10-dihydrophenanthrene ⁽⁹⁾ has given rise to significant improvements in conversion in short contact time liquefaction and in fluidised-bed pyrolysis ⁽⁹⁾. In contrast, removal of chloroform-extractable material has resulted in lower conversions in fluidised-bed pyrolysis ⁽¹⁰⁾ and in high temperature extraction with phenol ⁽¹¹⁾.

Clearly in the above cases where improved liquefaction yields have been achieved, the accessibility of solvents within the highly porous macromolecular structure of coals has been improved, particularly during the initial stages of liquefaction where retrogressive reactions need to be avoided. However, interpretation of the above phenomena in terms of changes in the macromolecular structure of coals is complicated by the fact some organic matter is being removed at the same time that conformational changes may be occurring and, in the case of polar solvents and pre-treatments at elevated temperatures, hydrogen bonds are being disrupted. Chlorobenzene has the advantage of extracting virtually no organic matter from coals ⁽¹²⁾ but it is non-polar and does not significantly disrupt hydrogen bonds at relatively low temperatures (<150°C). Therefore, in principle, it is possible to decouple the effects of conformational changes and extraction for this non-polar solvent. Indeed, it has already been demonstrated that chlorobenzene treatment markedly affects mass transfer phenomena in Upper Freeport coal ⁽¹³⁾ (Argonne Premium Coal Sample). Although the

CO₂ surface area remained constant at 180 m² g⁻¹, the time to reach equilibrium decreased from about 6 hours to only 5 minutes. Moreover, there was a significant change in the fractal dimension derived from SAXS. This parameter is a measure of the overall smoothness of the pores and varies between D=2 for a flat plane and D=3.0 for a surface so convoluted that it effectively fills a three dimensional volume. The change in D from 2.8 to 2.5 indicates that the chlorobenzene treatment is smoothing the pores and, as the CO₂ equilibration times demonstrate, this has a significant effect on mass transport within the macromolecular structure.

If the effect of chlorobenzene for Upper Freeport coal is general for most bituminous coals, significant changes in liquefaction behaviour can be anticipated due to the improved accessibility of solvents into the microporous structure and also the ability of coal-derived oil to possibly diffuse more effectively out of the remaining macromolecular framework. In this study, the effects of chlorobenzene treatment on short contact time tetralin extraction and dry hydrogenation with and without a dispersed sulphided molybdenum (Mo) catalyst for the Pittsburgh No. 8 Argonne Premium Coal Sample are reported and the results are discussed in light of the recent work on solvent pre-treatments⁽²⁻⁸⁾.

EXPERIMENTAL

Pittsburgh No.8 coal was treated in chlorobenzene under nitrogen for 1 week in a soxhlet apparatus. The extracted coal was then dried *in vacuo* at 50°C.

The following liquefaction experiments were conducted in duplicate on the original and chlorobenzene treated samples. For extractions in a hydrogen-donor solvent, 1 g of sample used and 2 g of tetralin were loaded into a microreactor which was submerged in a fluidised sandbath at 400°C for 15 minutes and was agitated using a flask shaker. The heat-up period for the thin-walled 1/2" O.D. microreactors was less than 2 minutes. After extraction, the reactor contents were recovered by filling the microreactor with dichloromethane (DCM) and placing it in an ultrasonic bath. The DCM washings were refluxed and filtered using phase separating paper and the DCM-solubles were recovered by evaporating the filtrate to dryness. The DCM-insolubles were weighed after drying *in vacuo* and were then refluxed in pyridine and filtered to determine the yield of pyridine-insolubles.

The dry or solvent-free hydrogenations were carried out with and without a sulphided Mo catalyst in a 9/16" O.D. microautoclave (*ca* 10 cm³) constructed of Autoclave Engineer high pressure fittings. For the catalytic experiments, the samples were loaded with 1% Mo (daf basis) by impregnation with a methanolic/water solution of ammonium dioxodithiomolybdate⁽¹⁴⁾. 0.3 g of sample was loaded into the microautoclave which was pressurised to 70 bar with hydrogen. A sandbath at 400°C was raised to fully submerge the microautoclave for 60 min., the heat-up period being *ca* 5 min. The reactor contents were recovered and fractionated as described above for the tetralin extractions.

RESULTS AND DISCUSSION

Tables 1 and 2 list the yields of DCM-solubles, pyridine-solubles/DCM-insolubles and pyridine-insolubles from the duplicate tetralin and hydrogenation experiments, respectively, carried out on the initial and chlorobenzene-treated coal, the repeatability being $\pm 1\%$ daf coal. The mean values are presented in Figures 1 and 2.

Tetralin Extractions

To highlight mass transfer effects during the initial stages of coal dissolution, tetralin was chosen as the solvent because it is largely in the vapour phase at 400°C and a relatively short contact time of 15 minutes was selected. Table 1 and Figure 1 indicate that chlorobenzene treatment has significantly improved the yield of DCM-solubles or oil. The fact that the total conversions to pyridine-solubles are extremely high would suggest that, for Pittsburgh No.8 coal which will undoubtedly soften to a considerable extent at 400°C, given that the free swelling index is 8, solvent accessibility is not too critical a factor affecting the initial dissolution. However, the vast increase of 20% daf coal in the yield of DCM-solubles clearly indicates improved solvent transport has been achieved with more hydrogen being available to promote the thermal breakdown of pyridine-soluble/DCM-insoluble material into oil.

The increase in oil yield is broadly comparable to that of 14% reported by Joseph ⁽⁴⁾ for tetralin extraction (with a hydrogen over-pressure) of an Illinois No.6 pre-treated with TBAH. Increases of only 5% were obtained for THF and methanol, but, nonetheless, pre-swelling with both these weakly-basic solvents increased the overall conversions to THF-solubles more than with TBAH. However, their boiling points are considerably lower than that of 132°C for chlorobenzene and, although some disruption of the hydrogen-bonding network in coals would undoubtedly have occurred as the coal swells to a significant extent, it is uncertain whether the glass transition temperature would have been lowered sufficiently to allow the coal to adopt a lower energy configuration. It is likely that the chlorobenzene treatment will also lead to significant improvements in primary conversions for non-hydrogen-donor polynuclear aromatic compounds in light of the fact THF extraction achieved this for a UK bituminous coal ⁽⁵⁾.

Hydrogenation

It is well-established that dispersed catalysts, such as sulphided Mo, significantly improve oil yields in solvent-free hydrogenation. At 400°C, yields of chloroform-solubles have been found to increase from 10-20% to 50-60% (daf basis) for bituminous and sub-bituminous coals upon catalyst addition ⁽⁵⁾. Interestingly, opposite conversion trends have been found after chlorobenzene treatment with and without catalyst for Pittsburgh No.8 coal (Table 2 and Figure 2). Without catalyst, the treatment increased the DCM-soluble yield from 19 and 31% and reduced the pyridine-insoluble yield from 40 to 20% indicating that transport of hydrogen gas into the depolymerising coal has been improved. Perhaps surprisingly at first sight, catalytic hydrogenation of the treated coal gave 25% less oil (DCM-solubles) and 12-13% more pyridine-solubles/DCM-insolubles and pyridine-insolubles (Table 2 and Figure 2).

The results with catalyst would appear to be contrary to both those of Joseph ⁽⁴⁾ and Artok *et al* ⁽⁸⁾ who both achieved increased yields in catalytic hydroliquefaction after pre-swelling in polar solvents. However, the experiments by Joseph were carried out in the presence of tetralin and the dominant effect could be the improved transport of the solvent into the macromolecular framework resulting in both more effective hydrogen donation and the transfer of dissociated hydrogen atoms from the catalyst particles. Further, the use of polar solvents which swell the coal considerably may have improved the dispersion of the Mo catalyst, although there is little evidence from hydropyrolysis studies on THF-extracted coals that this is the case ⁽¹⁵⁾. Without solvent, the transfer of hydrogen atoms is dependent on the bitumen or the oil generated by hydrogenation. However, it is likely that the transport of the oil out of the remaining macromolecular structure has also been improved by chlorobenzene treatment and, therefore, the effectiveness of the catalyst is reduced due to the less bitumen remaining in the pore structure to transport hydrogen atoms to reaction sites. Although Artok *et al* ⁽⁸⁾ found improved conversions in catalytic hydrogenation of Blind Canyon coal and two lignites, the experiments were conducted at 275°C and, not surprisingly at this low temperature, total conversions were less than 30% meaning that the amounts of oil available to transfer hydrogen atoms were small. Therefore, it is probable that the principal effect of pre-swelling in TBAH was to improve access of hydrogen gas into the macromolecular structure and thus limit retrogressive reactions.

General discussion

This investigation has reinforced other recent work ⁽²⁻⁸⁾ which indicated that pre-treatments can greatly enhance liquefaction yields, particularly in relatively low-severity regimes. However, much of the other work was concerned with pre-swelling coals in polar solvents where the dominant effect is undoubtedly the disruption of hydrogen bonding. Conversely, chlorobenzene is a low-swelling solvent and does not disrupt coal hydrogen bonding. However, as mentioned earlier, it acts as a plasticizer and, as such, lowers the glass transition temperature thus inducing conformational changes in the coal macromolecule during treatment. The nature of the conformational changes have yet to be elucidated but they are different to those induced by polar solvents and could well involve the disruption of non-covalent bonding between aromatic moieties. Indeed, our continuing research will investigate whether the conformational changes are general or occur to vastly differing extents for coals of varying rank and whether similar changes occur for other non-polar solvents, particularly polynuclear aromatic and hydroaromatic compounds found in vehicle solvents used in coal liquefaction. Circumstantial evidence discussed earlier would indeed suggest that this is the case ^(5,7) and more suitable contact between solvent and coal prior to liquefaction could prove to be extremely beneficial from a processing standpoint.

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Table 1 Tetralin Extraction Results

	DCM sols	% daf coal Pyr sols/DCM insols	Pyr sols
Initial coal	43.0	54.1	2.6
	42.7	55.1	1.7
CB Treated coal	62.9	32.0	3.0
	62.7	30.0	2.7

CB Treated coal is chlorobenzene extracted coal

Table 2 Hydrogenation Results

		DCM conv*	% daf coal DCM sols	Pyr sols/DCM insols	Pyr insols
Non- catalysed	Initial	22.0	17.5	30.7	40.5
		23.7	19.9	31.1	40.8
	CB Treated	30.1	26.3	45.8	17.4
		29.7	27.9	46.2	19.1
Catalysed	Initial	62.4	58.2	29.4	5.1
		62.1	57.9	30.9	5.4
	CB Treated	36.0	31.5	44.0	18.1
		35.5	31.4	42.6	17.4

* DCM sols +gas + water

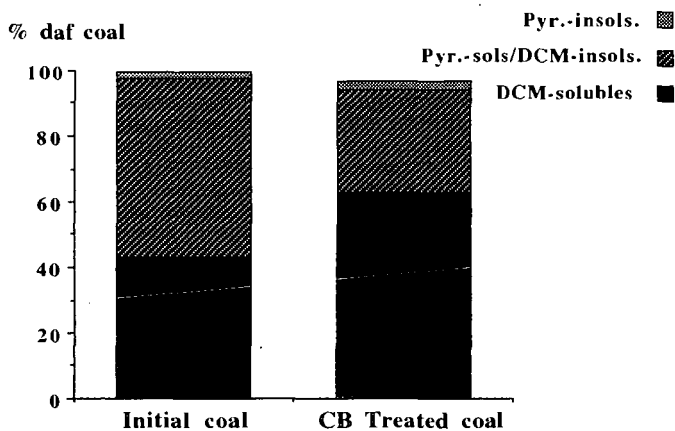


FIGURE 1 YIELDS FROM TETRALIN EXTRACTIONS

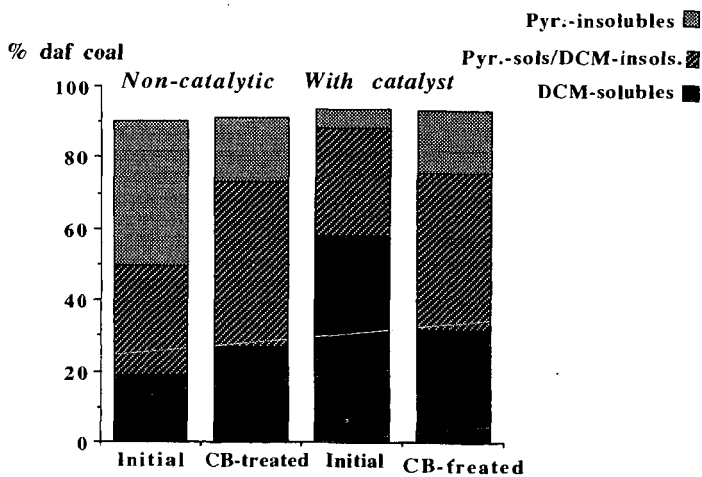


FIGURE 2 HYDROGENATION YIELDS